

# PATENT SPECIFICATION

(11) 1372787

1372787

- (21) Application No. 36341/72 (22) Filed 3 Aug. 1972  
 (31) Convention Application No. 170 631 (32) Filed 10 Aug. 1971 in  
 (33) United States of America (US)  
 (44) Complete Specification published 6 Nov. 1974  
 (51) International Classification D21H 3/44  
 (52) Index at acceptance D2B 36F2 36Q2 36QX 36QY 41A  
 (72) Inventors MERWIN F. HOOVER, PATRICIA G. GONGLOFF  
 and MEI HWA HWANG



## (54) NON-WOVEN FIBER PRODUCTS

(71) We, CALGON CORPORATION, a corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Pittsburgh, Pennsylvania, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with the treatment of fibres, particularly cellulosic fibers, with cationic polymeric additives.

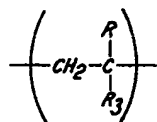
Prior to the present invention, many attempts had been made to combine the property of substantivity for the fibers with the ability to impart temporary wet strength, dry strength, high absorbency, flexibility and softness into a single additive for non-wovens including paper. The wet and dry strength characteristics are at odds with easy disposability (e.g. ready destruction in sewage systems) and with the desirability of rebroking the waste fibers. Consequently, previous efforts have been frustrated and results have been limited.

The use of amphoteric polymers containing carboxylic groups, amide groups, and quaternary groups in certain ratios to impart dry strength to cellulosic webs is disclosed in United States Patent No. 2,884,058. Improved wet and dry strength by the use of a thermo-setting methylol acrylamide diallylmelamine copolymer is disclosed in United States Patent No. 3,077,430.

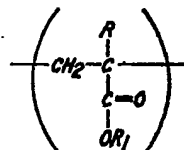
This invention is based on the discovery that certain cationic polymers, when added to aqueous suspensions of fibers, will impart to the fiber product the properties of wet strength, dry strength, absorbency, flexibility and softness. These properties are most important in the formation of hand towels, tissues and non-woven fabrics. In addition, the wet strength and dry strength properties are not so permanent as to cause disposability problems.

Moreover, the manufacturer can easily rebroke the waste from products made with our polymers.

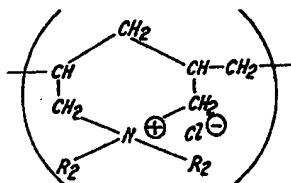
The polymers used in the process of the present invention are random linear copolymers, containing from 2 to 20 weight per cent of units of the formula:



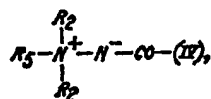
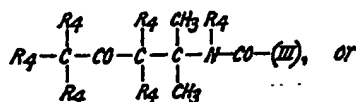
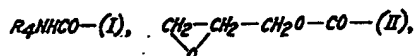
from 2 to 75 per cent by weight of units of the formula:



and from 15 to 95 per cent by weight of units of the formula:



in which formulae R is hydrogen or methyl, R<sub>1</sub> is a C<sub>1-18</sub> alkyl group, R<sub>2</sub> is a C<sub>1-4</sub> alkyl group, and R<sub>3</sub> is a group of formula:



in which  $R_2$  is as defined above,  $R_4$  is a hydrogen atom or a hydroxymethyl group, at least one  $R_4$  in at least half of the relevant groups being hydroxymethyl, and  $R_5$  is an alkyl group.

In accordance with the present invention, non-woven fiber products are made by forming an aqueous suspension of the fibers, adding to it a polymer of the type defined in the preceding paragraph, sheeting the fibers to form a web and drying the web.

The thermosetting residues in the polymers are derived from methylolated acrylamide, methylolated methacrylamide, glycidyl acrylate, glycidyl methacrylate, methylolated diacetone acrylamide and certain alkyl acrylic aminimides as described in U.S. Patents Nos. 3,485,806 and 3,527,802.

When using methylolated acrylamide or methacrylamide,  $R_4$  will have the formula (I). When preparing such polymers, several different methods are available. The first method is to mix the desired amounts of acrylate ester, dialkyl diallyl quaternary ammonium monomer and methylolacrylamide and/or methylolmethacrylamide monomers together and polymerize them using any of the well known solution, emulsion or suspension techniques. An alternative method is to prepare a polymer of the acrylate ester, the dialkyl diallyl quaternary ammonium compound and acrylamide and/or methacrylamide and then methylolate the acrylamide and/or methacrylamide with formaldehyde or a formaldehyde donor to the desired degree of methylation. Another alternative method of making this type of polymer is to prepare a polymer of the acrylate ester, the dialkyl diallyl quaternary ammonium compound, and acrylamide and/or methacrylamide. This polymer is then blended with formaldehyde or a formaldehyde donor and added to the pulp suspension, or alternatively the polymer and formaldehyde or formaldehyde donor are added separately to the pulp suspension. Using this third method, the methylation reaction occurs

when the paper is cured. It should be remembered that if a polymer which is completely methylolated is desired, the methylolacrylamide monomer should be used since it is extremely difficult to completely methylolate the monomer after it has been polymerized. In addition, at least 50 per cent of the acrylamide and/or methacrylamide groups must be methylolated in order to obtain desirable properties.

When using the glycidyl acrylate and/or methylacrylate as the thermosetting group,  $R_4$  will have the formula (II). When preparing such polymers, the desired amounts of acrylate ester, dialkyl diallyl quaternary ammonium monomer and glycidyl acrylate and/or glycidyl methacrylate are simply mixed together and polymerized using any of the well known solution, emulsion or suspension techniques. The resulting polymer is then used by adding a solution or emulsion of the polymer to the aqueous pulp suspension.

When utilizing the methylolated diacetone acrylamide as the thermosetting residue,  $R_4$  will have the formula (III). When preparing such polymers, the same general methods as described above for acrylamide are available. The fully methylolated diacetone acrylamide is a commercially available monomer and the other methylolated diacetone acrylamides may be easily prepared. When using the methylolated diacetone acrylamide, it is necessary that at least half of the diacetone acrylamide groups contain at least one methylolated group.

When using the lower alkyl acrylic aminimides as the source of the thermosetting functionality,  $R_5$  will have the formula (IV). When preparing such polymers, the desired amounts of acrylate ester, dialkyl diallyl quaternary ammonium monomer and acrylic aminimide are simply mixed together and polymerized using any of the well known solution, emulsion or suspension techniques. The resulting polymer is then used by adding a solution or emulsion of the polymer to the aqueous pulp suspension. The aminimide decomposes during the curing step to yield an isocyanate which bonds with the fiber.

The terpolymers described above are substantive to cellulosic fiber and can be cured at both alkaline and acid pH. They may be added to the paper in amounts, based on the weight of the cellulosic fiber, of from 0.25 per cent to about 2.0 per cent but, preferably, from 0.5 to 1.5 per cent. They may be added to the pulp suspension in the form of an emulsion or as a solution.

The terpolymers have been evaluated for their desired effect on fiber products. The general procedure used for evaluating the effect of the terpolymers on fiber properties was to prepare a stock furnish, incorporate the terpolymer into pulp suspension, form a hand sheet with the pulp and cure and test the hand sheet.

The furnish was made up according to a

standard for paper towelling. It consisted of 50 percent bleached softwood kraft and 50 percent hardwood kraft pulp. No filler, alum or any other material was added. The two types of pulp were separately disintegrated and beaten to 750—800 cc Schopper Riegler Freeness (550—600 cc Canadian Standard). Equal amounts of the two slush stocks were mixed together for use. The final pulp consistency was about 1.4 percent and had a pH of from 8 to 9.5.

The polymer solution or suspension to be tested was added to the aqueous pulp suspension prior to forming the hand sheet but after the pulp was beaten. The polymers were added in dosages of from 0.25 to 2.0 percent (based on weight of the dry pulp). They were added as 1 percent solutions or suspensions. The polymer was mixed with the pulp and gently stirred for a minute or more before being transferred to the hand sheet machine.

The treated pulp described above was transferred to a hand sheet machine and the cellulosic web was formed on the mould. In the hand sheet machine, the pulp was diluted to 0.12 percent consistency and the pH was adjusted as desired (that is either alkaline 8 to 9.5 or acidic 3.5 to 5). Hand sheets were then made from this pulp.

The hand sheets were then cured and tested. The curing was performed at temperatures ranging from 105° C. to 140° C. for twenty minutes or longer (until dry). The testing was performed as follows:

Dry and wet strength were measured according to TAPPI Standard Methods T22DM—69 and T4560S—68. They were reported as burst factor and breaking length. Absorbency was measured according to the TAPPI Standard Method T423TS—64 and reported as seconds required for the sheet to absorb 0.1 ml drop of distilled water. The softness was measured by the Gurley tester and reported as seconds required to leak 100 cc of air through the hand sheet at 300 pounds per square inch pressure. The longer the time the softer the paper. To evaluate the rebrokability, 56 grams of treated and cured hand sheets were torn and soaked overnight in 6,700 ml tap water with stirring. The pulp was then beaten in the beater and the rebrokability determined by freeness measurement.

As mentioned above, the polymers used in the invention may be prepared by using any of the well known polymerization techniques. If the resulting polymer is water-soluble, solution polymerization will be the easiest and preferred method of preparing the polymer. However, if the resulting polymer is water-insoluble, then either emulsion or suspension polymerization techniques will be used.

Example I below illustrates the preparation of a polymer for use in the invention having

a thermosetting group derived from methylolated acrylamide.

#### EXAMPLE I.

Synthesis of an Ethyl Acrylate - Dimethyl Diallyl Ammonium Chloride - Acrylamide (22.5/67.5/10 Weight Percent) Terpolymer.

#### Charge:

1. Water	145.30 grams	
2. Nonionic Surfactant Triton X305	17.20 grams	
3. Dimethyl Diallyl Ammonium Chloride (DMAAC) Solution (61.4 percent active)	220.00 grams	75
4. General Electric Anti-foam 10	0.33 ml	80
5. EDTA	0.05 grams	
6. Acrylamide (dissolve in 50 grams water)	20.00 grams	
7. Ethyl Acrylate	45.00 grams	
8. Potassium Persulphate	1.35 grams	85
9. Sodium Bisulphite	0.50 grams	

#### Procedure.

The water, surfactant, anti-foam agent, EDTA and DMAAC were mixed together in a one-liter flask fitted with a stirrer, condenser, purge tube, thermometer and two additional funnels. The solution was purged for one hour at room temperature. The ethyl acrylate and the acrylamide solutions were put into separate addition funnels and 1/10 of each solution was added to the flask after the one-hour purge. The monomer solution was stirred while being heated to 40° C. The purge tube was raised to blanket the reaction and the persulfate and bisulfite added. The remaining monomers were slowly dripped in so that 1/3 of the acrylamide and 2/3 of the acrylate had been added by one hour after the catalyst addition. The exotherm had reached 50.5° C. by that time and the emulsion had begun to thicken. During the next fifteen minutes, the rest of the acrylate and acrylamide were rapidly added, and the emulsion was allowed to exotherm. Two and one half hours after initiation, the exotherm reached a maximum temperature at 86° C. The total reaction time was 3½ hours. The final viscous blue-white latex was diluted to a 25 per cent solids emulsion which had a Brookfield viscosity of 1,600 cps and a pH = 6.0.

#### Methylation of Terpolymer.

The terpolymer prepared by the method above was methylolated with 10 percent para-formaldehyde by weight. The theoretical result would be a polymer containing 10 percent by weight methylol acrylamide, but because of structural hindrance, due mainly to chain coiling, all acrylamide sites were probably not reacted. The most effective procedure for methylation is given below.

Reactants.		(improved hand) to the final tissue. For example, polymers derived from acrylates such as octadecyl methacrylate and isodecyl methacrylate impart softness but decrease absorbency and have a somewhat deleterious effect on the other desired properties. On the other hand, polymers derived from acrylates such as methylmethacrylate, ethyl acrylate, and butyl acrylate do not deleteriously affect the other properties but do not always impart the desired amount of water repellency and softness. Therefore, the acrylate portion may be a mixture of two or more different acrylate esters which will give the desired properties.	30
1.	Terpolymer (25 percent active)	50.00 grams	
2.	Paraformaldehyde	1.25 grams	
5 3.	Sodium hydroxide solution (N/2)	as needed	
4.	Buffer (pH = 7.4) of NaOH and monopotassium phosphate	72.00 grams	35
10	Procedure.		40
	The 25 percent active solids emulsion was heated to 55—60° C. in a water bath and the pH of the latex adjusted to 9.0. The formaldehyde was added and stirred while the pH was again brought up to 9.0 every five minutes. By fifteen minutes after the formaldehyde had been added, the emulsion had thickened to a jelly-like ball. The latex was immediately removed from the bath and enough buffer added to bring the total weight of the latex to 125 grams giving a 10 percent active solids solution. The thickened latex was dissolved in the buffer with a brief stirring on the Heller mixer.		
15			45
20			50
25	Polymers in which the acrylate ester contained from 1 to 18 carbon atoms have been prepared. The use of the higher acrylate ester imparts water repellency as well as softness		55
	In addition, polymers in which the dialkyl diallyl ammonium monomer contained various alkyl groups have been prepared. However, dimethyl diallyl ammonium chloride or diethyl diallyl ammonium chloride is preferred.		
	The following three tables illustrate the results of Burst Strength, Tensile Strength, Absorbency and Softness tests on paper incorporating one of the polymers, including a comparison with papers containing no such polymer. The polymer was a terpolymer of 67.5 percent dimethyl diallyl ammonium chloride, 22.5 percent ethyl acrylate and 10 percent acrylamide which was methylolated after polymerization according to the procedure described in Example I.		

TABLE I  
BURST STRENGTH (MULLEN)

TREATMENT			BURST STRENGTH (MULLEN)						
Resin Added (% of Dry Pulp)	pH	Curing Temperature (°C.)	Curing Time	Basis Weight (G/M <sup>2</sup> )	Dry Burst Factor	% Increase Over Control	Wet Burst Factor	% Wet Over Dry Sheet	% Wet Over Dry Control
0	9.0	120	1 Hour	47.6	15.4	0	4.4	28.0	28.0
1.0	4.5	120	1 Hour	47.6	34.5	124.4	6.1	17.7	39.7
0.5	9.0	120	1 Hour	48.5	20.7	34.4	4.6	22.3	29.9
0.5	9.0	105	Overnight	48.2	—	—	7.6	—	49.4
0.5	4.5	120	1 Hour	48.2	25.9	68.2	5.9	22.8	38.4
0.5	4.5	105	Overnight	48.1	27.1	76.0	7.4	27.3	48.1
1.0	9.0	120	1 Hour	46.9	22.4	45.5	6.6	29.5	42.8
1.0	9.0	105	Overnight	47.4	26.0	68.8	8.2	31.6	53.3
1.0	4.5	120	1 Hour	48.5	26.6	72.7	7.1	26.8	46.1
1.0	4.5	105	Overnight	46.6	27.8	80.5	8.3	29.9	54.0

TABLE II

TENSILE STRENGTH

TREATMENT			TENSILE STRENGTH						
Resin Added (% of Dry Pulp)	pH	Curing Temperature (°C.)	Curing Time	Basis Weight (G/M <sup>2</sup> )	Dry Breaking Length	% Increase Over Control	Wet Breaking Length	% Wet Over Dry Sheet	% Wet Over Dry Control
0	9.0	120	1 Hour	47.6	4900	0	63	1.29	1.3
1.0	4.5	120	1 Hour	47.6	6182	26.2	1129	1.8	23.0
0.5	9.0	120	1 Hour	48.5	4983	17.0	467	9.4	9.5
0.5	9.0	105	Overnight	48.2	—	—	583	—	12.0
0.5	4.5	120	1 Hour	48.2	5312	8.4	508	9.5	10.4
0.5	4.5	105	Overnight	48.1	5372	9.6	761	14.2	15.5
1.0	9.0	120	1 Hour	46.9	5610	14.5	509	9.1	10.4
1.0	9.0	105	Overnight	47.4	5109	4.3	718	14.1	14.7
1.0	4.5	120	1 Hour	48.5	5233	6.8	671	12.9	13.7
1.0	4.5	105	Overnight	46.6	5790	18.2	1002	17.4	20.5

TABLE III

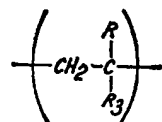
TREATMENT		Curing Temperature (°C.)	Curing Time	Basis Weight (G/M <sup>2</sup> )	Absorbency (0.1 ml Distilled Water) Second	Softness (Gurley) Second
Resin Added (% of Dry Pulp)	pH					
0	9.0	120	1 Hour	47.6	29.7	33.8
1.0	4.5	120	1 Hour	47.6	110	32.4
0.5	9.0	120	1 Hour	48.5	45	32.6
0.5	9.0	105	Overnight	48.2	57	34.8
0.5	4.5	120	1 Hour	48.2	64	32.4
0.5	4.5	105	Overnight	48.1	58	34.2
1.0	9.0	120	1 Hour	46.9	73	30.0
1.0	9.0	105	Overnight	47.4	79	32.2
1.0	4.5	120	1 Hour	48.5	83	30.1
1.0	4.5	105	Overnight	46.6	140	30.7

The rebrokability test for this sample showed that it was possible to disintegrate the terpolymer treated paper. The original pulp freeness was reached after a slight heating of the shredded paper.

Similar tests have been performed with other polymeric compositions of the invention. The results indicate that the terpolymers are substantive to the fibers and improve dry and wet strength at either alkaline or acid pH. In addition, the terpolymers provide increased absorbency and improved softness. Finally, all of the polymers are rebrokable to the original pulp freeness without an unduly extensive or expensive treatment.

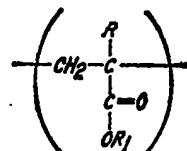
#### WHAT WE CLAIM IS:—

1. A process for making non-woven fiber products by forming an aqueous suspension of the fibers, adding to the fiber suspension a random linear polymer containing from 2 to 20 weight per cent of units of the formula

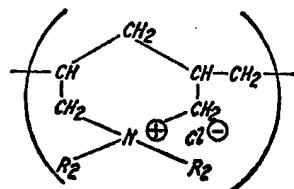


from 2 to 75 per cent by weight of units of the formula:

25

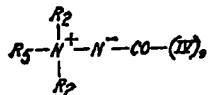


and from 15 to 95 per cent by weight of units of the formula:



in which formulae R is hydrogen or methyl, R<sub>1</sub> is a C<sub>1-18</sub> alkyl group, R<sub>2</sub> is a C<sub>1-4</sub> alkyl group, and R<sub>3</sub> is a group of formula:

30



Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1974.  
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.

This Page is inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record

## BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURED OR ILLEGIBLE TEXT OR DRAWING
- ☒ SKEWED/SLANTED IMAGES
- ☒ COLORED OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REPERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images  
problems checked, please do not report the  
problems to the IFW Image Problem Mailbox**